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(54) A METHOD OF BONDING RUBBER TO METAL

- (71) We, TRW Inc., a corporation of the State of Ohio, United States of America, of One Space Park, Redondo Beach, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention is a modification of that described and claimed in specification No. 1,193,301; it relates to the bonding of metal to rubber, and provides a method of bonding a metal surface to a rubber surface comprising applying to one or both surfaces a coating of a mixture comprising a polyfunctional polydiene prepolymer having at least 50% of its olefinic unsaturation in the form of pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain, a polyfunctional organic chain extender capable of reacting with the functional groups on the polydiene prepolymer and a peroxide free-radical initiator capable of heat-curing the mixture to a thermoset resin, pressing the surfaces together with the mixture therebetween, causing or permitting the mixture to react by chain extension to form an elastomeric resin having the free-radical initiator dispersed therethrough, and subsequently forming an adhesive bond between the surfaces by heat-curing the elastomeric resin to a thermoset resin. In one modification, heat is applied to the mixture between the surfaces to effect chain extension and heat curing in a single step; in another reaction proceeds to the elastomer stage before the rubber and metal are brought together for the compression and heat curing operation.
- 40 The resins employed in this invention belong to the family of thermoset and curable elastomeric resins discussed in specifications Nos. 1,193,301, 1,193,734, 1,195,565, 1,195,566 and 1,194,723. It is to be understood that the additional polyfunctional polyether and other prepolymers, and the internally plasticized forms described in these specifications may be employed in the practice of this invention as well as the described chain extenders and peroxide free radical initiators enumerated therein.
- 50 The polydiene prepolymers used preferably have at least 80% of their olefinic unsaturation as pendant vinyl groups on alternate carbon atoms of the backbone carbon chain, and preferably have a molecular weight from 500 to 3000. The preferred polydiene is 1,2-polybutadiene, although 3,4-polyisoprene is also suitable. Difunctional prepolymers characterized by chain terminal substitution are preferred, but other polyfunctional prepolymers having functional groups located at opposite ends of the molecule, but not necessarily the terminal positions, may be used. While a dihydroxy substituted prepolymer is generally preferred, mainly from the standpoint of ease of reactivity, a dicarboxy substituted compound or other polydienic prepolymer having chemically functional groups preferably terminally positioned will also be satisfactory.
- 55 Selection of a suitable organic chain extender is dependent upon the functional groups on the prepolymers. Where the functional groups on the prepolymers are hydroxyl, the chain extender should preferably be a diisocyanate, diacid halide, diacid, or diester. Where the functional groups on the prepolymer are carboxy, the chain extender should preferably be a diepoxide, diimine, diol, or diaziridine. The aliphatic or aromatic organic chain extenders are preferably difunctional, but may contain more than two functional groups.
- 60 In preparing these resins, the polyfunctional organic chain extender should be mixed in an approximately stoichiometric amount to the polydiene prepolymer. Adjustments are necessary when other ingredi-

ents such as copolymeric prepolymers or internal plasticizers are employed, but approximately the stoichiometric quantity of the organic chain extender with respect to the prepolymeric ingredients is the preferred amount. The peroxide is generally employed in an amount within the range of 2% to 6%. It will be appreciated that larger or smaller amounts of the peroxide may be employed and that the optimum amount is dependent upon, among other things, the particular peroxide initiator used, the polydiene prepolymer employed, and the chain extender selected for the reaction.

After the ingredients have been mixed, the polymeric liquid should desirably be degassed in vacuum to remove entrapped air and volatile impurities. A chain extending reaction proceeds at room temperature or moderately elevated temperatures to produce an elastomeric intermediate material having the peroxide free radical initiator molecularly dispersed throughout. The chain extension reaction may be catalyzed to reduce reaction temperature or time by catalytic agents which are standard art, providing they do not interfere with the subsequent curing step, which is preferably conducted at 150°F to 400°F.

Surface preparation of the metal and the rubber is accomplished according to the teachings of adhesive art, e.g., the surfaces are carefully cleaned. One procedure which has been proven effective involves cleaning the rubbery surface with a high boiling naptha solvent and subsequently buffing. In many cases, chemical pretreatment of metal surfaces which provides for chemical adhesion of the mixture to the surface will markedly enhance the strength of the adhesive bond.

The initial mixture may be applied to the surfaces by any suitable means, e.g. — spraying, painting, etc. If the mixture has a thicker consistency than is desired, solvents can be used to thin the mixture, however, generally they must be removed by volatilization prior to adhering. An exception to the volatilization requirement exists in the use of styrene which becomes an internal plasticizer to reduce the viscosity of the reacting ingredients; in this case styrene serves as an internal plasticizer in the cured product.

Because of the formation of the intermediate elastomeric material, joining of the rubber and metal surfaces may be accomplished in a number of ways. In one method, one or each surface is coated with the liquid mixture and the surfaces are pressed together. The article is then subjected to elevated temperatures in the range of 150°F to 400°F whereupon a hard, strong, chemically resistant, adhesive bond is formed; if desired the mixture may be permitted to

react to the elastomer stage before the heat curing step. In another method, each surface is coated with the liquid mixture but the surfaces are not joined. Upon exposure to room or moderately elevated temperatures the liquid composition undergoes a chain extension step in which an elastomeric material is formed. At a later time, the two coated surfaces may be placed together and cured at a temperature range between 150°F and 400°F with the application of moderate mechanical pressure, e.g.—between 10 and 100 psig is adequate. By this means, the surfaces may be coated at one site and shipped to another site where they may be joined by the mere application of heat and pressure without the inconvenience normally associated with application of adhesives. In a further method one surface, preferably the metal surface, is coated with the liquid mixture which is allowed to proceed to the elastomeric intermediate stage. Then at a later time, the coated surface is joined with the clean uncoated other surface and the joint is subsequently cured at an elevated temperature under pressure.

The time required for the final bond to form will vary according to resin formulation and temperature. The bonding time required is governed by the period required to effect a full heat cure. Generally, this time may vary from approximately ten seconds to ten minutes.

It can be appreciated that the described adhesive resin can provide greater versatility than heretofore possible because of the stepwise curing property. In addition to the attractive features such as chemical interaction with the rubber surface and wettability of metal surfaces the final adhesive resin exhibits excellent oxidative, chemical, hydrolytic, and thermal stability. Such properties are attractive where the adhesive is to be used to bond solid rubber tires to metal rims or rubber cleats to metal tracked vehicles. Other applications may involve leak tight seals for electrical contacts made through rubber housing, or where the article is exposed to the severe conditions of liquid nitrogen tetroxide, caustic solutions, or degrading solvents.

WHAT WE CLAIM IS:—

1. An article having a metal surface with a rubber surface bonded thereto by means of a thermoset resin obtainable by forming a mixture comprising a polyfunctional polydiene prepolymer having at least 50% of its olefinic unsaturation in the form of pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain, a polyfunctional organic chain extender capable of reacting with the functional groups on the polydiene prepolymer and a peroxide free-radical initiator capable of heat-curing

the mixture to a thermoset resin and heating the mixture to cure it to a thermoset resin.

2. An article according to claim 1 wherein the polyfunctional polydiene prepolymer is dihydroxy substituted 1,2-polybutadiene or 3,4-polyisoprene.

3. An article according to claim 2 wherein the polyfunctional organic chain extender is a diisocyanate, diacid halide, dicarboxy, or diester substituted aliphatic or aromatic compound.

4. An article according to claim 1 wherein the polyfunctional polydiene prepolymer is dicarboxy substituted 1,2-polybutadiene or 3,4-polyisoprene.

5. An article according to claim 4 wherein the polyfunctional organic chain extender is a diepoxide, diamine, dihydroxy, or diaziridine substituted aliphatic or aromatic compound.

6. An article according to any of claims 1 to 5 wherein the peroxide free-radical initiator is an aromatic or aliphatic peroxide.

7. An article according to any of claims 1 to 6 wherein the mixture contains in addition a polyfunctional polyether prepolymer.

8. An article according to any of claims 1 to 7 wherein the mixture additionally includes styrene.

9. A method of bonding a metal surface to a rubber surface comprising applying to one or both surfaces a coating of a mixture comprising a polyfunctional polydiene prepolymer having at least 50% of its olefinic unsaturation in the form of pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain, a polyfunctional organic chain extender capable of reacting with the functional groups on the polydiene prepolymer and a peroxide free-radical initiator capable of heat-curing the mixture to a thermoset resin, pressing the surfaces together with the mixture therebetween, and forming an adhesive bond between the surfaces by heat-curing the mixture to a thermoset resin.

10. A method of bonding a metal surface to a rubber surface comprising applying to one or both surfaces a coating of a mixture comprising a polyfunctional polydiene prepolymer having at least 50% of its olefinic unsaturation in the form of pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain, a polyfunctional organic chain extender capable of reacting with the functional groups on the polydiene prepolymer and a peroxide free-radical initiator capable of heat-curing the mixture to a thermoset resin, pressing the surfaces together with the mixture therebetween, causing or permitting the mixture to react by chain extension to form an elastomeric resin having the free-radical initiator

dispersed therethrough, and subsequently forming an adhesive bond between the surfaces by heat-curing the elastomeric resin to a thermoset resin.

11. A method of bonding a metal surface to a rubber surface comprising applying to one or both surfaces a coating of a mixture comprising a polyfunctional polydiene prepolymer having at least 50% of its olefinic unsaturation in the form of pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain, a polyfunctional organic chain extender capable of reacting with the functional groups on the polydiene prepolymer and a peroxide free-radical initiator capable of heat-curing the mixture to a thermoset resin, causing or permitting the mixture to react by chain extension to form an elastomeric resin having the free-radical initiator dispersed therethrough, and subsequently pressing the surfaces together with the elastomeric resin therebetween and forming an adhesive bond between the surfaces by heat-curing the elastomeric resin to a thermoset resin.

12. A method according to claim 9, 10 or 11 wherein the polydiene prepolymer has a molecular weight of from 500 to 3000.

13. A method according to any of claims 9 to 12 wherein the polydiene prepolymer has at least 80% of its olefinic unsaturation as pendant vinyl groups on alternate carbon atoms of the backbone chain.

14. A method according to any of claims 9 to 13 wherein the polyfunctional polydiene prepolymer is dihydroxy substituted 1,2-polybutadiene or 3,4-polyisoprene.

15. A method according to claim 14 wherein the polyfunctional organic chain extender is a diisocyanate, diacid halide, dicarboxy, or diester substituted aliphatic or aromatic compound.

16. A method according to any of claims 9 to 13 wherein the polyfunctional polydiene prepolymer is dicarboxy substituted 1,2-polybutadiene or 3,4-polyisoprene.

17. A method according to claim 16 wherein the polyfunctional organic chain extender is a diepoxide, diamine, dihydroxy, or diaziridine substituted aliphatic or aromatic compound.

18. A method according to any of claims 9 to 17 wherein the peroxide free-radical initiator is an aromatic or aliphatic peroxide.

19. A method according to any of claims 9 to 18 wherein the mixture contains in addition a polyether polyfunctional prepolymer.

20. A method according to any of claims 9 to 19 wherein the mixture additionally contains styrene.

21. A method according to any of claims 9 to 20 wherein the heat-curing temperature is 150 to 400°F.

22. A method according to any of claims 9 to 21 wherein the surfaces are pressed together under a pressure of from 10 to 100 psig.
- 5 23. An article having a metal or rubber surface coated with a resin obtainable by forming a mixture comprising a polyfunctional polydiene prepolymer having at least 50% of its olefinic unsaturation in the form of pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain, a polyfunctional organic chain extender capable of reacting with the functional groups on the polydiene prepolymer and a 15 peroxide free-radical initiator capable of heat-curing the mixture to a thermoset resin and causing or permitting the mixture to react by chain extension to form an elastomeric resin having the free-radical initiator dispersed therethrough. 20
24. An article having a metal surface bonded to a rubber surface by a method according to any of claims 9 to 22.
25. An article according to claim 1 having a metal surface bonded to a rubber surface substantially as hereinbefore described. 25
26. A method according to claim 9 for bonding a metal surface to a rubber surface substantially as hereinbefore described.

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